PB86-208675

Organochlorine Contaminants of Wintering Ducks Foraging on Detroit River Sediments

(U.S.) Environmental Research Lab.
Duluth, Grosse Ile, MI

1985

U.S. Department of Commerce
National Technical Information Service
NTIS.

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/J-85/419	2. PB86-208675
4. TITLE AND SUBTITLE Organochlorine Contaminants of Wintering Ducks Foraging on Detroit River Sediments. (Journal Version)	5. REPORT DATE 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) V. Elliott Smith[1], John M. Spurr[2], John C. Filkins[3] and Jody J. Jones.[4]	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS 1-Raytheon Service Co., 9311 Groh Rd., Grosse Ile, MI 2-Clayton Environmental Consul., Inc., 25711 Southfield Rd, Southfield, MI 3-USEPA, Grosse Ile, MI; 4-Univ. of Maine, Orono, ME	10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. CR810232-01
12. SPONSORING AGENCY NAME AND ADDRESS Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Duluth, MN 55804	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA-600/3

15. SUPPLEMENTARY NOTES
Published in J. Great Lakes Res. 11(3):231-246, Internat. Assoc. Great Lakes Res., 1985.

16. ABSTRACT

*ABSTRACT. Organochlorine analysis was performed on carcasses of 13 diving ducks from a 1981 wintering population that foraged on contaminated sediments in the lower Detroit River. Mean total PCB concentrations were 10 mg/kg for seven lesser scaups (*Aythya affinis*), 11 mg/kg for three greater scaups (*A. marila*), and 7.6 mg/kg for three goldeneyes (*Bucephala clangula*). Highest mean levels of other residues were measured for hexachlorobenzene (1.7 mg/kg) in goldeneyes, and trans-nonachlor (0.33 mg/kg) and 4,4'-DDE (1.3 mg/kg) in greater scaup. Quantitative analysis of 72 PCB congeners also was applied to water, seston, sediment, benthic oligochaetes, and carp from the same site. Principal congeners in most of the samples included some of the more toxic and persistent PCBs. Results of a multivariate analysis indicated that ratios of more conservative to less conservative PCBs did not vary significantly among ducks ($\alpha = .05$), but differed from those in carp, oligochaetes, and sediment. For the February through March period of fat mobilization, concentrations of total PCB in lipid were inversely correlated with percent lipid ($r = 0.76$) in ducks. The percentage of conservative PCBs increased slightly. The distribution and partitioning of organochlorines, including toxic PCB congeners, varied considerably within this water column-sediment-fauna ecosystem. Estimates of toxic exposure based on total PCB values may be unreliable.*

ADDITIONAL INDEX WORDS: Polychlorinated biphenyls, toxic substances, chlorinated hydrocarbons, benthos.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18 DISTRIBUTION STATEMENT Release to public.	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES 17
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (Rev. 4-77)

REPRODUCED BY NATIONAL TECHNICAL INFORMATION SERVICE U.S. DEPARTMENT OF COMMERCE SPRINGFIELD, VA. 22161

NTIS is authorized to reproduce and sell this report. Permission for further reproduction must be obtained from the copyright owner.

EPA/600/J-85/419
JOURNAL ARTICLE

J. Great Lakes Res. 11(3):231-246
Internat. Assoc. Great Lakes Res., 1985

ORGANOCHLORINE CONTAMINANTS OF WINTERING DUCKS FORAGING ON DETROIT RIVER SEDIMENTS

V. Elliott Smith[1] and John M. Spurr[2]
Cranbrook Institute of Science
P.O. Box 801
Bloomfield Hills, Michigan 48013

John C. Filkins
U.S. Environmental Protection Agency
Large Lakes Research Station
9311 Groh Road
Grosse Ile, Michigan 48138

Jody J. Jones
University of Maine
Orono, Maine 04469

*ABSTRACT. Organochlorine analysis was performed on carcasses of 13 diving ducks from a 1981 wintering population that foraged on contaminated sediments in the lower Detroit River. Mean total PCB concentrations were 10 mg/kg for seven lesser scaups (*Aythya affinis*), 11 mg/kg for three greater scaups (*A. marila*), and 7.6 mg/kg for three goldeneyes (*Bucephala clangula*). Highest mean levels of other residues were measured for hexachlorobenzene (1.7 mg/kg) in goldeneyes, and trans-nonachlor (0.33 mg/kg) and 4,4'-DDE (1.3 mg/kg) in greater scaup. Quantitative analysis of 72 PCB congeners also was applied to water, seston, sediment, benthic oligochaetes, and carp from the same site. Principal congeners in most of the samples included some of the more toxic and persistent PCBs. Results of a multivariate analysis indicated that ratios of more conservative to less conservative PCBs did not vary significantly among ducks ($\alpha = .05$), but differed from those in carp, oligochaetes, and sediment. For the February through March period of fat mobilization, concentrations of total PCB in lipid were inversely correlated with percent lipid ($r = 0.76$) in ducks. The percentage of conservative PCBs increased slightly. The distribution and partitioning of organochlorines, including toxic PCB congeners, varied considerably within this water column-sediment-fauna ecosystem. Estimates of toxic exposure based on total PCB values may be unreliable.*
ADDITIONAL INDEX WORDS: Polychlorinated biphenyls, toxic substances, chlorinated hydrocarbons, benthos.

INTRODUCTION

The Detroit River, connecting Lakes St. Clair and Erie, is one of the world's busiest waterways, which passes through a highly industrialized area of the United States and Canada (Fig. 1). Among the principal contaminants found in Detroit River sediments are organochlorines (Fallon and Horvath 1983), including polychlorinated biphenyls (PCBs). Due to their hydrophobic nature and stability, PCBs tend to collect and persist in organic sediments (Choi and Chen 1976, Hague *et al.* 1974; Crump-Wiesner *et al.* 1973). To the degree that PCBs and other contaminants accumulate in sediments and associated benthos, they become

[1]Present address: Raytheon Service Company, Large Lakes Research Station, 9311 Groh Road, Grosse Ile, Michigan 48138

[2]Present address: Clayton Environmental Consultants, Inc., 25711 Southfield Road, Southfield, Michigan 48075

FIG. 1. Mud Island study site on the lower Detroit River, Michigan.

available at higher concentrations to larger bottom-foraging fauna. Thus polluted sediments in many nearshore areas may act as reservoirs of "in-place" contaminants which continue to enter the food chain long after point sources of pollution are controlled.

Each winter, thousands of migratory waterfowl congregate on the Detroit River, attracted by areas of shallow, ice-free water. These include diving ducks, such as scaups and goldeneyes, which forage on plant and animal matter in the sediments. During 1980–82, Drobney *et al.* (1982) studied the food habits and nutritional status of 169 lesser scaups (*Aythya affinis*), greater scaups (*A. marila*), and goldeneyes (*Bucephala clangula*) wintering on the lower Detroit River. This was part of a study designed to evaluate the effects of winter navigation on survival of waterfowl. The collections presented us with an opportunity to study the possible uptake and accumulation by ducks of selected organochlorines, including PCB congeners, from polluted sediment. In part, our objective was to identify and compare complex PCB mixtures in these ducks and in their benthic food supply at a foraging site. We thought that Detroit River sediment might be an important source of PCBs, even for transient waterfowl. If so, then distinctive patterns of certain congeners in sediment might be found also in local benthos, ducks and other bottom feeders. Another related goal was to examine the relationship between lipid and PCB concentrations in the ducks during this period of increased fat metabolism.

Weekly counts of waterfowl along the lower Detroit River near its junction with Lake Erie (Fig. 1) showed concentrations of up to 24,000 ducks and geese in late January, 1980, which declined steadily to approximately 5,000 birds in late March, just prior to the final northward migration (Drobney *et al.* 1982). It is likely that local populations in March included transient ducks from wintering grounds farther south.

Of the 13 ducks analyzed in this study, 11 were collected at Mud Island; the remaining two were collected 8 km southward on the river (Fig. 1). The study site was in shallow (1–3 m) water on the downstream side of Mud Island, where aquatic macrophytes grow abundantly in the soft bottom during the summer. Sediments there are finely textured with a high organic content. Immediately after ducks were collected at this site, their gut contents were removed and preserved in formalin for later identification (Drobney *et al.* 1982). Their diets were found to include a wide variety of invertebrate and plant materials. However, the bulk of their food consisted of oligochaete worms (including *Tubifex sp.*) and tubers of *Vallisneria* sp. and *Potamogeton* sp., two species of aquatic flowering plants. The percentages of plant and animal matter found in gut contents are summarized in Table 1 (from Drobney *et al.*, 1982). Their results show that pollution-tolerant oligochaetes may be an important winter food for diving ducks in the

TABLE 1. Aggregate percent of animal and plant ( ) matter in gut contents of 169 ducks (after Drobney et al. *1982).*

	Male	Female	Both
Common Goldeneye *Bucephala clangula*	27.3 (72.6)	44.0 (55.9)	35.6 (64.8)
Lesser Scaup *Aythya affinis*	24.6 (75.3)	33.1 (66.9)	27.9 (72.1)
Greater Scaup *Aythya marila*	12.7 (87.3)	28.4 (71.6)	18.6 (81.6)

Detroit River, as they were for old squaw ducks (*Clangula hyemalis*) in Milwaukee Harbor (Rofritz 1977). Oligochaetes were reported to have a higher caloric content than other benthos studied by Cummins and Wuycheck (1971).

Since Mud Island was a prominant feeding area for ducks, we also sampled other components of this system: unfiltered water, filterable seston, surficial sediment, oligochaetes, and adult carp (*Cyprinus carpio*), the last representing a bottom-feeding fish. Sediment samples collected represented only recently deposited material likely to be available to foraging ducks and fish. At Mud Island this was defined as the upper 4-cm zone of a sediment core in which 65% of the total PCB mass occurred at nearly uniform concentrations. Within the next 5–9 cm interval of sediment depth, the PCB concentration rapidly declined. Biological mixing of surficial sediments and associated contaminants has been documented elsewhere in the Great Lakes (Robbins 1982) and in laboratory microcosms (Karickhoff and Morris 1985).

Studies have shown that the composition of PCB mixtures in environmental samples is highly variable due to differences in the chemical and biological behavior of congeners (Safe 1980, Hutzinger *et al.* 1974). Certain PCBs are more persistent (i.e., conservative) than others, as indicated by the similarity of these congener ratios in the environment to those in commercial PCB mixtures (Ballschmiter and Zell 1980, Ballschmiter *et al.* 1978). We evaluated all of the possible ratios of congeners in Mud Island sediment and fauna, and selected six congeners that were involved most frequently in the most consistent ratios. The distribution of these "conservative" congeners was compared to that of PCBs as a whole.

METHODS

A detailed description of the field and laboratory methods is included in a more comprehensive report on the Detroit River studies (Smith *et al.* 1984). The following is a brief summary of methods.

Each water sample (12 L), collected in four 3.8-L brown glass jugs, was extracted by partitioning twice with dichloromethane in a 15:1 ratio. Combined extracts were concentrated, transferred into n-hexane, dried through sodium sulfate columns, and evaporated under nitrogen to volumes of 2–10 mL, as adapted from standard EPA procedures (Thompson 1974). Excess lipids were removed by treating 2-mL extracts with concentrated sulfuric acid, and subsequently freezing the aqueous layer in an acetone-dry ice bath (Murphy 1972). Cleaned extracts in hexane were stored temporarily in sealed glass ampules (8°C, dark).

Seston was collected by pressure filtration (<35 kpa) through glass fiber filters (nominally, 0.6 μm porosity). Filters, stored temporarily in glass jars with acetone, were exhaustively extracted by Soxhlet with n-hexane-acetone (1:1), transferred into n-hexane, and processed as above.

Oligochaetes were hand-picked from grab samples (Ponar dredge) of sediment, after the larger particles were collected by washing the mud through a 0.5 mm mesh bronze wire sieve (U.S. #30). Frozen oligochaetes (5 g) were mixed with anhydrous sodium sulfate (1:3) and exhaustively extracted by Soxhlet with n-hexane:dichloromethane (1:1) for 6 hours. Extracts were processed as for water and seston samples.

Sediment cores, approximately 15 cm long, were collected by pushing a pole-mounted aluminum tube (5 cm diameter) into the bottom. Three cores were sectioned at 1 cm intervals and equivalent sections were combined. Sediments were exhaustively extracted by Soxhlet with n-hexane-acetone (1:1) and processed as above. The final extracts were treated with reactive copper to remove sulfur (Environment Canada 1979). Based on preliminary analysis, the upper four 1-cm sections were shown to have similar concentrations of total PCB. Extracts of these sections were combined as representing the mixed zone of sediment.

Extracts of monthly water and seston samples collected during July–November 1982 were combined to form one sample of each. Eleven oligochaete samples from the same period were also combined. Three sediment samples, collected on 14 December 1982, were combined.

Carp were gill-netted on 17 September 1982, and stored frozen, prior to grinding and homogenizing the whole fish. Ducks, collected by shotgun during January–March 1980, were eviscerated, defeathered, and the head and feet were removed prior to freezing. Homogenized aliquots (20 g) of duck or fish tissue were mixed with sodium sulfate (3:1), and exhaustively extracted with n-hexane-dichloromethane (1:1). Extracts were processed as above. Total lipids in carp and duck tissue were determined gravimetrically after drying at room temperature a 1-mL aliquot of the 10-mL final extract. All solvents used were of "pesticide grade" from Burdick and Jackson, Muskegon, Michigan. All glassware was cleaned rigorously with deter-

gents and solvent rinses, followed by baking at 580°C. Glassware assemblies were refluxed or rinsed again with solvents before use.

For organochlorine analyses we used a Varian 3700 capillary column gas chromatograph fitted with dual Ni^{63} electron capture detectors, autosamplers, and 50 m × 0.2 mm (i.d.) SE-54 thin film, fused silica columns. Chromatographic conditions were as described elsewhere (Smith *et al.* 1985). Component peaks were baseline-corrected prior to quantitation. Individual PCB congeners were analyzed with reference to a standard mixture of Aroclors 1016, 1254, and 1260, in which 95 congeners had been identified and 72 of these quantitated using synthetic PCB standards (Mullin *et al.* 1983, Mullin *et al.* 1984). Octachloronaphthalene was used as an internal standard to verify retention times. Homolog and total PCB values were based on the appropriate summations of congener values. Other organochlorines were similarly quantitated.

Glassware and solvent blank values for Mud Island water samples averaged 5.7% and 4.5% of sample values for PCBs and other organochlorines, respectively. Corresponding blank values for PCBs in sediment, oligochaetes, and ducks averaged less than 3% of those in the samples. Analytical precision calculated for total PCBs in nine replicate duck samples was 6.48% RSD. For 11 replicate analyses of an Aroclor 1254 standard, the precision was 10.8% RSD. The 72 congener values that were summed for total PCBs represented 84% of the true mass, based on later analysis of the same Aroclor 1254 standard. The Aroclor contained 15 more congeners that were not accounted for by standards at the time of analysis.

RESULTS AND DISCUSSION

Characteristics of the 13 duck samples analyzed are given in Table 2 according to R. D. Drobney (1983, personal communication, University of Maryland, Frostburg, MD). The content of water, fat, and lean dry mass in each case is given as a percentage of the dressed weight (head, feet, feathers, and viscera removed). Most of the variation in dressed weight was due to differences in fat and water content; the percentage of lean dry mass, largely protein, was relatively constant at 21.5–28.2% of dressed weight. We also measured lipid (fat) dry weight for an aliquot of the crude extract used for organochlorine analysis. This value was used here to express the concentration of contaminants per unit lipid. Comparison of these

TABLE 2. Characteristics and tissue composition of 13 ducks analyzed (after Drobney 1983, unpublished data, University of Maryland, Frostburg, MD)

Species	Coll. No.	Wk Coll.*	Age/ Sex	Total Wt. (G)	Dressed Wt. (G)[1]	% Water[2]	% Fat[3]	% Lean Dry Mass[4]
Lesser Scaup	8	7	jv. F	969.9	710.4	54.2	23.3	22.5
Aythya affinis	13	7	jv. F	1,029.1	746.8	51.0	27.5	21.5
	53	10	ad. F	974.5	787.8	54.5	18.6	26.9
	59	11	ad. F	778.7	487.2	65.4	6.7	28.0
	72	12	ad. F	710.4	528.2	59.9	13.3	26.8
	79	12	jv. F	714.9	519.1	62.4	12.0	25.6
	82	12	ad. F	710.4	482.7	51.8	23.5	24.7
Greater Scaup	47	10	ad. F	910.7	601.1	62.9	8.9	28.2
Aythya marila	50	10	ad. F	1,006.3	614.7	54.4	22.8	22.8
	66	11	jv. M	969.9	642.1	57.7	17.2	25.1
Goldeneye	1	6	ad. F	796.9	555.5	54.8	23.0	22.2
Bucephala clangula	2	7	jv. M	1,293.2	979.0	49.9	27.3	22.8
	29	8	jv. F	860.6	592.0	62.2	11.9	25.9

[1]Wet weight minus head, feet, feathers, and viscera.
[2]Recovered by freeze drying.
[3]Recovered by petroleum ether extraction.
[4]Remaining after water and fat extracted.
*Weeks 1–12 are Jan.–March 1980

two sets of lipid measurements per unit of tissue showed agreement within 9% of the lower value, despite the difference in extraction solvents used (Methods and Table 2).

Table 3 summarizes the concentrations of various organochlorines, including total PCBs, in ducks and other compartments of the Mud Island system. The water, seston, sediment, and oligochaete values represent composites of samples collected over a 5-month period. For carp (n = 9) and ducks (n = 13) the mean and standard deviation are shown, along with the range and percent occurrence of each contaminant. The total PCB values represent a summation of congener concentrations: 72 different congeners were quantitated in carp, and 68 in ducks. The variability of total PCB concentrations in carp and duck species, expressed as %RSD, was: carp, 48.5; lesser scaup, 47.2; greater scaup, 17.3; goldeneye, 23.6.

Mean concentrations of total PCB adjusted for lipid (PCB/% lipid) in ducks were: lesser scaup, 79 mg/kg; greater scaup, 89 mg/kg; goldeneye, 38 mg/kg. Although total PCB values were higher for both scaup species relative to goldeneye, the survey of gut contents from 169 ducks (Table 1) indicates that a higher proportion of animal matter, mainly oligochaetes, was consumed by goldeneyes. However, the gut contents were not available for organochlorine analysis. The seston PCB concentration in the water column (5.2 mg/kg) suggests a greater input of PCBs to the bottom than was indicated by the concentration in sediment (0.63 mg/kg).

At lower concentrations alpha- and gamma-BHC (hexachlorocyclohexane) had a distribution similar to that of PCB in the carp and ducks (Table 3). Hexachlorobenzene concentrations were relatively high in ducks, and particularly in goldeneyes (mean, 1.7 mg/kg). *Cis*- and *trans*-chlordanes were found in scaup ducks (means, 0.0025–0.0097 mg/kg), but not in goldeneyes. Concentrations of *cis*- and *trans*-nonachlor (means, 0.013–0.33 mg/kg) were measured in most ducks of all three species. Of the DDT group, 4,4′-DDE levels were highest (means, 0.48–1.3 mg/kg), especially in greater scaups. Other organochlorines that occurred less consistently were beta- and delta-BHC, heptachlor epoxide, and alpha- and gamma-chlordane. All standards of organochlorines reported here were shown to be stable under the acid conditions used to clean extracts (Murphy 1972).

High resolution gas chromatography/mass spectroscopy analysis, applied to extracts of a female greater scaup (no. 50) and female goldeneye (no. 1) by Kuehl (1983, personal communication, EPA/ERL-Duluth, MN), confirmed the presence of trichlorobiphenyls through nonachlorobiphenyls, *cis*- and *trans*-chlordane, *cis*- and *trans*-nonachlor, 4,4′-DDE and hexachlorobenzene, other chlorinated benzenes, and octachlorostyrene. Low levels of chlorinated cyclohexanes (alpha-, beta-, gamma-, and delta-BHC) and heptachlor epoxide, reported here, were not confirmed by mass spectroscopy.

Concentrations of the individual congeners comprising PCB mixtures in sediment, oligocheaetes, carp, and ducks from Mud Island are shown in Table 4. Included are the homolog values representing groups of congeners with two to nine chlorines per molecule. Congeners in Table 4 are identified by their structures and by peak numbers (Ballschmiter and Zell 1980). The percent composition by congener of PCBs in all 13 ducks is summarized in Figure 2. Only 18 of the 72 congeners reported accounted for 90% of the total PCB mass in scaups and goldeneyes combined.

The advantages of congener-specific analysis of PCBs have been widely recognized (Mullin *et al.* 1984, Mullin *et al.* 1983, Duinker *et al.* 1980, Ballschmiter and Zell 1980). One important benefit is that concentrations of potentially toxic congeners can be measured individually. Toxicities measured with respect to the induction of aryl hydrocarbon hydroxylase (AHH) enzymes and other effects have been reported (Safe *et al.* 1982), and structural characteristics of these congeners are known (Ballschmiter *et al.* 1978).

Among the potentially more toxic PCB congeners which occur as major components in ducks, oligochaetes, carp, and sediments from Mud Island are nine tri-, tetra-, penta-, hexa- and heptachlorobiphenyls (Table 4, asterisks). These account for averages of 28.3% of the total PCB mass in lesser scaups, 31.0% in great scaups, and 36.8% in goldeneyes. In each species, over 84% of this fraction is represented by only three congeners: 2,3′,4,4′,5-pentachlorobiphenyl, 2,2′,3,4,4′,5′-hexachlorobiphenyl, and 2,2′,3,3′,4,4′,5-heptachlorobiphenyl. These congeners, respectively, caused embryotoxicity in chickens (Ax and Hansen 1975), accumulation of rat liver porphyrins (Stonard and Grieg 1976), and AHH enzyme induction (Parkinson and Safe 1981).

Previous work (Haseltine and Prouty 1980, Custer and Heinze 1980, Heath *et al.* 1972) has indicated that ducks may be relatively insensitive to

TABLE 3. Organochlorine concentrations (wet weight basis) in Mud Island samples.

Compound	Composites				Carp *Cyprinus carpio*	Ducks		
	Water ng/L (n = 1)	Seston mg/kg (n = 1)	Sediment mg/kg (n = 1)	Oligochaetes mg/kg (n = 1)	mg/kg (n = 9)	Lesser Scaup *Aythya affinis* mg/kg (n = 7)	Greater Scaup *Aythya marila* mg/kg (n = 3)	Goldeneye *Bucephala clangula* mg/kg (n = 3)
Total PCB	45.	5.2	0.63	0.44	16. ± 7.7(100) 7.6 to 31.	10. ± 4.9(100) 2.7 to 20.	11. ± 2.0(100) 8.3 to 13.	7.6 ± 1.8(100) 4.2 to 11.
Hexachlorobenzene	0.75	0.22	0.0031	0.0036	0.10 ± 0.43 (100) 0.028 to 0.17	0.33 ± 0.12(100) 0.15 to 0.77	0.37 ± 0.17(100) 0.16 to 0.78	1.7 ± 1.2(100) 0.16 to 4.8
Alpha BHC	12.	0.041	0.0002	0.0019	0.045 ± 0.018(100) 0.016 to 0.072	0.016 ± 0.013(71) 0.0046 to 0.039	0.013 ± 0.0050(100) 0.004 to 0.023	0.0098 ± 0.0041(100) 0.0044 to 0.017
Beta BHC	0.11	0.0089	0.0003	–	0.0023(11)	0.013 ± 0.0031(43) 0.0085 to 0.016	0.012 ± 0.0019(100) 0.0086 to 0.015	–
Gamma BHC (Lindane)	1.4	0.012	–	–	0.0063 ± 0.0036(100) 0.0028 to 0.016	0.0050 ± 0.0021(43) 0.0024 to 0.0075	0.0016 ± 0.0004(67) 0.0011 to 0.0022	0.0020(33)
Delta BHC	0.064	0.023	–	–	0.0012(11)	–	0.0024(33)	–
Heptachlor Epoxide	0.056	0.0045	–	–	0.0037 ± 0.0006(33) 0.0026 to 0.0047	0.014 ± 0.0023(29) 0.011 to 0.017	0.014 ± 0.0015(67) 0.012 to 0.017	–
Trans-Chlordane	0.19	0.031	0.0011	0.0018	0.11 ± 0.041(100) 0.035 to 0.19	0.0025 ± 0.0003(57) 0.0021 to 0.0028	0.0029(33)	–
Cis-Chlordane	0.22	0.028	0.0016	0.0027	0.18 ± 0.072(100) 0.048 to 0.31	0.0097 ± 0.0032(43) 0.0057 to 0.014	0.0048 ± 0.0014(100) 0.0030 to 0.0072	–
Trans-Nonachlor	0.26	0.045	0.0044	0.0024	0.16 ± 0.066(100) 0.077 to 0.26	0.17 ± 0.076(100) 0.056 to 0.28	0.33 ± 0.031(67) 0.28 to 0.37	0.081 ± 0.0071(67) 0.071 to 0.091
Cis-Nonachlor	0.038	0.0068	0.0003	0.0007	0.035 ± 0.014(100) 0.014 to 0.062	0.023 ± 0.0097(100) 0.0034 to 0.054	0.049 ± 0.020(100) 0.025 to 0.074	0.013 ± 0.0089(100) 0.0056 to 0.028
4,4′ DDE	0.57	0.10	0.012	0.0059	0.38 ± 0.15(100) 0.21 to 0.74	0.80 ± 0.33(100) 0.29 to 1.2	1.3 ± 0.25(100) 0.84 to 1.6	0.48 ± 0.18(100) 0.29 to 0 72
4,4′ DDD	0.85	0.16	0.023	0.015	0.48 ± 0.26(100) 0.16 to 1.1	0.093 ± 0.027(100) 0.039 to 0.16	0.14 ± 0.045(100) 0.070 to 0.18	0.080 ± 0.024(100) 0.061 to 0.12
4,4′ DDT	0.39	0.059	0.012	–	0.023 ± 0.012(56) 0.010 to 0.046	0.025(14)	0.040 ± 0.0094(67) 0.027 to 0.054	0.040(33)

Mean ± Standard Deviation (% occurrence)
Range

TABLE 4. PCB composition (wet weight basis) by congener and homolog of Mud Island samples. Compounds of potentially greater toxicity are indicated (*).

PCB Congener		Sediment (1–4 cm) (mg/kg) (n = 1)	Oligochaetes (Composite) (mg/kg) (n = 1)	Carp *Cyprinus carpio* (mg/kg) (n = 9)	Lesser Scaup *Aythya affinis* (mg/kg) (n = 7)	Greater Scaup *Aythya marila* (mg/kg) (n = 3)	Goldeneye *Bucephala clangula* (mg/kg) (n = 3)
Peak #	Structure						
4	2,2′	0.0065	–	0.66 (11)	–	–	0.077 (33)
7	2,4	0.0019	–	0.015 ± 0.0089 (33) 0.0066 - 0.029	0.015 ± 0.0046 (57) 0.0061 - 0.024	0.014 ± 0.0047 (100) 0.0082 - 0.020	–
	Sum of Di-chlorobiphenyls	0.0084	–	0.24 ± 0.29 (33) 0.0066 - 0.69	0.015 ± 0.0046 (57) 0.0061 - 0.024	0.014 ± 0.0047 (100) 0.0082 - 0.020	0.077 (33)
17	2,2′,4	0.013	0.0045	0.36 ± 0.69 (100) 0.032 - 2.3	–	–	–
18	2,2′,5	0.016	0.0061	0.15 ± 0.14 (100) 0.025 - 0.52	–	0.036 (33)	0.041 (33)
22	2,3,4′	0.0028	0.0016	0.022 ± 0.015 (100) 0.0064 - 0.056	0.0053 ± 0.004 (29) 0.0047 - 0.0059	–	–
26	2,3′,5	0.0033	–	0.065 ± 0.095 (100) 0.012 - 0.33	0.0032 (14)	0.0064 (33)	0.0098 (33)
31	2,4′,5	0.044	0.025	0.36 ± 0.30 (100) 0.084 - 1.2	0.63 ± 0.28 (71) 0.31 - 1.1	0.71 ± 0.15 (67) 0.50 - 0.93	0.45 ± 0.13 (100) 0.23 - 0.68
33	2′,3,4	0.013	0.0072	0.092 ± 0.052 (100) 0.036 - 0.21	0.018 ± 0.0058 (100) 0.0090 - 0.026	0.0216 ± 0.0057 (100) 0.013 - 0.026	0.029 (33)
	Sum of Tri-chlorobiphenyls	0.092	0.045	1.0 ± 1.3 (100) 0.022 - 4.6	0.47 ± 0.34 (100) 0.20 - 1.1	0.51 ± 0.37 (100) 0.026 - 0.94	0.48 ± 0.11 (100) 0.27 - 0.68
40	2,2′,3,3′	0.0052	–	0.041 ± 0.024 (89) 0.0080 - 0.091	–	0.014 (33)	0.012 (33)
42	2,2′,3,4′	0.0071	0.0034	0.098 ± 0.075 (100) 0.021 - 0.26	0.0083 (14)	–	0.0098 (33)
43	2,2′,3,5	0.0010	–	0.021 ± 0.013 (89) 0.0090 - 0.050	–	0.011 (33)	–
44	2,2′,3,5′	0.017	0.0078	0.26 ± 0.17 (100) 0.10 - 0.63	0.013 ± 0.0004 (29) 0.012 - 0.013	0.010 ± 0.0039 (67) 0.0048 - 0.016	–
45	2,2′,3,6	0.0030	0.0020	.046 ± 0.038 (100) 0.012 - 0.14	–	–	–
46	2,2′,3,6′	0.0017	0.0013	0.013 ± 0.0082 (56) 0.0058 - 0.028	0.011 (14)	–	–
47	2,2′,4,4′	0.0048	0.0031	0.14 ± 0.11 (100) 0.027 - 0.41	0.12 ± 0.083 (100) 0.027 - 0.28	0.10 ± 0.039 (100) 0.063 - 0.16	0.063 ± 0.017 (100) 0.029 - 0.091
48	2,2′,4,5	0.0038	0.0018	0.058 ± 0.018 (44) 0.025 - 0.11	0.023 ± 0.0021 (29) 0.020 - 0.026	0.045 (33)	0.0088 (33)
49	2,2′,4,5′	0.014	0.0072	0.34 ± 0.22 (100) 0.14 - 0.79	0.039 ± 0.024 (100) 0.014 - 0.085	0.030 ± 0.0069 (100) 0.019 - 0.046	0.022 ± 0.0064 (67) 0.013 - 0.032
52	2,2′,5,5′	0.021	0.012	0.47 ± 0.31 (100) 0.17 - 1.0	0.048 ± 0.024 (100) 0.014 - 0.082	0.038 ± 0.0081 (67) 0.027 - 0.049	0.021 ± 0.0054 (67) 0.014 - 0.029
53	2,2′,5,6′	0.0053	0.0025	0.048 ± 0.041 (44) 0.016 - 0.12	–	–	0.0091 (33)
63	2,3,4′,5	0.0010	–	0.028 ± 0.018 (89) 0.010 - 0.062	0.030 ± 0.015 (100) 0.013 - 0.058	0.030 ± 0.0035 (100) 0.023 - 0.036	0.024 ± 0.0046 (100) 0.020 - 0.031
64	2,3,4′,6	0.0085	0.0029	0.19 ± 0.12 (100) 0.077 - 0.42	0.014 ± 0.0058 (86) 0.0067 - 0.022	0.011 ± 0.0013 (67) 0.0094 - 0.013	0.010 ± 0.0015 (67) 0.0083 - 0.013

TABLE 4. continued

Peak #	PCB Congener Structure	Sediment (1–4 cm) (mg/kg) (n = 1)	Oligochaetes (Composite) (mg/kg) (n = 1)	Carp *Cyprinus carpio* (mg/kg) (n = 9)	Lesser Scaup *Aythya affinis* (mg/kg) (n = 7)	Greater Scaup *Aythya marila* (mg/kg) (n = 3)	Goldeneye *Bucephala clangula* (mg/kg) (n = 3)
70	2,3',4',5	0.022	0.0087	0.16 ± 0.069 (100) 0.059 - 0.30	0.046 ± 0.026 (100) 0.011 - 0.093	0.044 ± 0.0050 (100) 0.036 - 0.055	0.039 ± 0.0002 (100) 0.038 - 0.039
74	2,4,4',5	0.0086	0.0048	0.23 ± 0.16 (100) 0.095 - 0.62	0.30 ± 0.13 (100) 0.11 - 0.50	0.26 ± 0.027 (100) 0.21 - 0.30	0.19 ± 0.048 (100) 0.15 - 0.26
81*	3,4,4',5	0.0006	0.0003	0.021 ± 0.012 (100) 0.010 - 0.045	0.31 ± 0.017 (100) 0.0046 - 0.053	0.046 ± 0.016 (100) 0.033 - 0.071	0.017 ± 0.0002 (100) 0.016 - 0.017
	Sum of Tetra-chlorobiphenyls	0.12	0.058	2.09 ± 1.3 (100) 0.84 - 4.7	0.64 ± 0.31 (100) 0.22 - 1.2	0.57 ± 0.066 (100) 0.49 - 0.65	0.38 ± 0.048 (100) 0.28 - 0.46
82	2,2',3,3',4	0.0032	0.0006	0.030 ± 0.016 (100) 0.0071 - 0.061	0.0083 ± 0.0041 (86) 0.0031 - 0.014	0.0074 ± 0.0022 (100) 0.0036 - 0.011	0.0097 ± 0.0003 (67) 0.0093 - 0.010
84	2,2',3,3',',6	0.014	0.0066	0.32 ± 0.16 (100) 0.17 - 0.62	0.10 (14)	0.053 (33)	0.067 (33)
87	2,2',3,4,5'	0.0098	0.0027	0.21 ± 0.13 (100) 0.096 - 0.51	0.027 ± 0.0018 (29) 0.024 - 0.029	–	–
95	2,2',3,5',6	0.046	0.027	1.2 ± 0.57 (100) 0.62 - 2.2	0.24 ± 0.18 (71) 0.027 - 0.62	0.17 ± 0.026 (100) 0.14 - 0.21	0.15 ± 0.018 (100) 0.14 - 0.18
97	2,2',3',4,5	0.0043	0.0018	0.059 ± 0.030 (100) 0.019 - 0.10	0.015 ± 0.0080 (100) 0.0046 - 0.032	0.013 ± 0.0017 (100) 0.011 - 0.017	0.014 ± 0.0020 (100) 0.0087 - 0.017
100	2,2',4,4',6	0.0013	0.0011	0.0083 ± 0.0040 (56) 0.0038 - 0.014	0.013 ± 0.0072 (71) 0.0060 - 0.027	0.0073 (33)	0.019 ± 0.0004 (67) 0.018 - 0.019
101	2,2',4,5,5'	0.018	0.011	0.52 ± 0.28 (100) 0.28 - 1.1	0.075 ± 0.040 (100) 0.026 - 0.16	0.082 ± 0.012 (100) 0.061 - 0.096	0.062 ± 0.0057 (100) 0.050 - 0.071
114*	2,3,4,4',5	0.0005	–	0.011 ± 0.0050 (78) 0.0055 - 0.021	0.017 ± 0.0077 (100) 0.0045 - 0.030	0.017 ± 0.0037 (100) 0.014 - 0.023	0.010 ± 0.0006 (100) 0.0091 - 0.011
118*	2,3',4,4',5	0.017	0.0069	0.42 ± 0.26 (100) 0.19 - 1.1	0.52 ± 0.26 (100) 0.15 - 0.98	0.59 ± 0.10 (100) 0.48 - 0.73	0.36 ± 0.041 (100) 0.29 - 0.43
119	2,3',4,4',6	0.0007	–	0.015 ± 0.0080 (100) 0.0058 - 0.030	0.012 ± 0.0051 (86) 0.0047 - 0.025	0.021 ± 0.0075 (100) 0.011 - 0.029	0.010 ± 0.0036 (67) 0.0048 - 0.015
	Sum of Penta-chlorobiphenyls	0.12	0.058	2.8 ± 1.4 (100) 1.4 - 5.7	0.91 ± 0.54 (100) 0.20 - 2.0	0.98 ± 0.15 (100) 0.85 - 1.2	0.66 ± 0.067 (100) 0.55 - 0.78
128*	2,2',3,3',4,4'	0.0046	0.0021	0.13 ± 0.064 (100) 0.058 - 0.26	0.18 ± 0.094 (100) 0.040 - 0.34	0.24 ± 0.054 (100) 0.18 - 0.31	0.13 ± 0.036 (100) 0.086 - 0.18
129	2,2',3,3',4,5	0.0009	0.0006	0.029 ± 0.014 (100) 0.014 - 0.060	–	–	–
131	2,2',3,3',4,6	–	–	0.30 ± 0.081 (22) 0.19 - 0.42	0.089 ± 0.030 (71) 0.030 - 0.15	0.17 (33)	0.054 (33)
134	2,2',3,3',5,6	0.0015	0.0009	0.041 ± 0.019 (100) 0.022 - 0.078	–	–	–
136	2,2',3,3',6,6'	0.0088	0.0034	0.19 ± 0.075 (100) 0.11 - 0.31	0.016 (14)	0.021 (33)	
137	2,2',3,4,4',5	0.0026	0.0075	0.073 ± 0.031 (100) 0.040 - 0.14	0.091 ± 0.053 (100) 0.015 - 0.19	0.13 ± 0.021 (67) 0.10 - 0.16	0.062 ± 0.012 (100) 0.052 - 0.080
138*	2,2',3,4,4',5'	0.027	0.026	1.0 ± 0.66 (100) 0.37 - 2.66	0.95 ± 0.40 (100) 0.23 - 1.6	1.3 ± 0.055 (67) 1.3 - 1.4	0.71 ± 0.13 (100) 0.40 - 0.92
141	2,2',3,4,5,5'	0.0075	0.0063	0.28 ± 0.15 (100) 0.12 - 0.58	0.040 ± 0.016 (100) 0.014 - 0.060	0.063 ± 0.021 (100) 0.033 - 0.084	0.035 ± 0.0056 (100) 0.025 - 0.045

TABLE 4. continued

Peak #	PCB Congener Structure	Sediment (1-4 cm) (mg/kg) (n = 1)	Oligochaetes (Composite) (mg/kg) (n = 1)	Carp *Cyprinus carpio* (mg/kg) (n = 9)	Lesser Scaup *Aythya affinis* (mg/kg) (n = 7)	Greater Scaup *Aythya marila* (mg/kg) (n = 3)	Goldeneye *Bucephala clangula* (mg/kg) (n = 3)
144	2,2',3,4,5',6	0.0055	0.0036	0.20 ± 0.10 (100) 0.094 - 0.41	0.019 ± 0.0083 (100) 0.0071 - 0.035	0.022 ± 0.0033 (100) 0.017 - 0.030	0.020 ± 0.0024 (100) 0.017 - 0.024
146	2,2',3,4',5,'	0.0054	0.0045	0.23 ± 0.11 (100) 0.095 - 0.44	0.27 ± 0.14 (100) 0.052 - 0.50	0.36 ± 0.078 (100) 0.24 - 0.43	0.19 ± 0.070 (100) 0.09 - 0.31
149	2,2',3,4',5',6	0.020	0.020	0.88 ± 0.50 (100) 0.37 - 2.0	0.19 ± 0.051 (86) 0.074 - 0.23	0.23 ± 0.047 (100) 0.16 - 0.27	0.16 ± 0.031 (100) 0.089 - 0.21
151	2,2',3,5,5',6	0.0082	0.0091	0.36 ± 0.15 (56) 0.16 - .60	0.025 ± 0.0097 (86) 0.0091 - 0.043	0.021 ± 0.0058 (100) 0.012 - 0.028	0.025 ± 0.0040 (100) 0.018 - 0.032
153	2,2',4,4',5,5'	0.045	0.044	1.9 ± 1.0 (100) 0.75 - 4.1	1.9 ± 0.94 (100) 0.40 - 3.7	2.5 ± 0.50 (100) 1.8 - 2.9	1.4 ± 0.61 (100) 0.66 - 2.5
156[d]	2,3,3',4,4',5	0.0024	0.0016	0.061 ± 0.024 (89) 0.031 - 0.10	0.090 ± 0.044 (86) 0.021 - 0.17	0.098 ± 0.0091 (100) 0.082 - 0.11	0.064 ± 0.018 (100) 0.043 - 0.094
158*	2,3,3',4,4',6	0.0029	0.0025	0.11 ± 0.044 (79) 0.054 - 0.18	0.11 ± 0.040 (86) 0.031 - 0.16	0.15 ± 0.023 (100) 0.12 - 0.18	0.073 ± 0.015 (67) 0.052 - 0.093
	Sum of Hexa-chlorobiphenyls	0.14	0.13	5.3 ± 2.8 (100) 2.3 - 11.	3.8 ± 1.8 (100) 0.89 - 7.0	4.7 ± 1.4 (100) 2.6 - 5.9	2.9 ± 0.86 (100) 1.5 - 4.4
170*	2,2',3,3',4,4',5	0.031	0.025	0.89 ± 0.49 (78) 0.40 - 1.8	1.0 ± 0.54 (100) 0.20 - 2.1	1.0 ± 0.17 (100) 0.75 - 1.2	0.73 ± 0.23 (100) 0.28 - 1.1
172	2,2',3,3',4,5,5'	0.0026	0.0024	0.082 ± 0.038 (100) 0.033 - 0.14	0.094 ± 0.041 (100) 0.017 - 0.16	0.12 ± 0.018 (100) 0.090 - 0.13	0.060 ± 0.018 (100) 0.027 - 0.091
173	2,2',3,3',4,5,6	0.0002	0.0003	0.011 ± 0.0051 (100) 0.0047 - 0.021	0.0032 ± 0.0017 (57) 0.0014 - 0.0061	0.0029 (33)	0.0055 ± 0.0021 (67) 0.0026 - 0.0084
174	2,2',3,3',4,5,6'	0.013	0.013	0.41 ± 0.20 (100) 0.18 - 0.75	0.10 ± 0.039 (100) 0.036 - 0.14	0.14 ± 0.024 (100) 0.11 - 0.16	0.098 ± 0.017 (100) 0.058 - 0.12
175	2,2',3,3',4,5',6	0.0007	0.0009	0.022 ± 0.0090 (100) 0.012 - 0.038	0.020 ± 0.0078 (86) 0.0044 - 0.029	0.024 ± 0.0051 (100) 0.019 - 0.031	0.019 ± 0.0031 (100) 0.015 - 0.022
176	2,2',3,3',4,6,6'	0.0025	0.0071	0.063 ± 0.030 (100) 0.020 - 0.14	0.035 ± 0.025 (86) 0.0086 - 0.073	0.037 ± 0.021 (67) 0.0068 - 0.067	0.038 ± 0.0075 (100) 0.028 - 0.046
177	2,2',3,3',4',5,6	0.0084	0.0060	0.23 ± 0.11 (100) 0.089 - 0.42	0.18 ± 0.057 (100) 0.049 - 0.23	0.20 ± 0.042 (100) 0.16 - 0.26	0.12 ± 0.033 (100) 0.070 - 0.18
180	2,2',3,4,4',5,5'	0.039	0.031	1.2 ± 0.66 (100) 0.44 - 2.5	1.4 ± 0.79 (100) 0.24 - 3.0	1.3 ± 0.26 (100) 0.86 - 1.7	0.92 ± 0.32 (100) 0.38 - 1.5
183	2,2',3,4,4',5',6	0.014	0.014	0.37 ± 0.18 (100) 0.14 - 0.69	0.44 ± 0.22 (100) 0.090 - 0.86	0.48 ± 0.10 (100) 0.32 - 0.58	0.30 ± 0.082 (100) 0.15 - 0.44
185	2,2',3,4,5,5',6	0.0017	0.0018	0.077 ± 0.038 (100) 0.032 - 0.16	0.015 ± 0.0055 (100) 0.0053 - 0.021	0.020 ± 0.0046 (100) 0.013 - 0.024	0.017 ± 0.0012 (100) 0.016 - 0.019
187	2,2',3,4',5,5',6	0.0092	0.024	0.67 ± 0.38 (100) 0.23 - 1.6	0.51 ± 0.20 (100) 0.15 - 0.82	0.54 ± 0.048 (100) 0.46 - 0.59	0.39 ± 0.096 (100) 0.17 - 0.54
189*	2,3,3',4,4',5,5'	–	0.0006	0.016 ± 0.0084 (100) 0.0067-0.034	0.018 ± 0.0071 (100) 0.0041-0.030	0.020 ± 0.0038 (100) 0.014-0.028	0.014 ± 0.0081 (100) 0.0045-0.024
191	2,3,3',4,4',5',6	0.0037	0.0019	0.048 ± 0.021 (100) 0.022-0.083	0.052 ± 0.025 (100) 0.010-0.096	0.058 ± 0.0098 (100) 0.045-0.069	0.032 ± 0.011 (100) 0.016-0.051
193	2,3,3',4',5,5',6	0.0014	0.0036	0.054 ± 0.027 (79) 0.023-0.11	0.061 ± 0.025 (86) 0.013-0.095	0.061 ± 0.0078 (100) 0.048-0.071	0.037 ± 0.0090 (100) 0.017-0.051
	Sum of Hepta chlorobiphenyls	0.11	0.12	3.6 ± 2.0 (100) 1.5-8.3	3.8 ± 1.9 (100) 0.79-7.4	3.8 ± 0.64 (100) 2.7-4.6	2.6 ± 0.72 (100) 1.2-3.9

TABLE 4. continued

Peak #	PCB Congener Structure	Sediment (1-4 cm) (mg/kg) (n = 1)	Oligochaetes (Composite) (mg/kg) (n = 1)	Carp *Cyprinus carpio* (mg/kg) (n = 9)	Lesser Scaup *Aythya affinis* (mg/kg) (n = 7)	Greater Scaup *Aythya marila* (mg/kg) (n = 3)	Goldeneye *Bucephala clangula* (mg/kg) (n = 3)
194	2,2',3,3',4,4',5,5'	0.0043	0.0034	0.10 ± 0.044 (89) 0.052-0.17	0.17 ± 0.10 (100) 0.033-0.40	0.15 ± 0.022 (100) 0.11-0.19	0.11 ± 0.035 (100) 0.060-0.17
195	2,2',3,3',4,4',5,6	0.0022	0.0017	0.056 ± 0.028 (89) 0.026-0.11	0.079 ± 0.040 (100) 0.016-0.16	0.065 ± 0.0095 (100) 0.049-0.081	0.049 ± 0.015 (100) 0.025-0.075
198	2,2',3,3',4,5,5',6	0.0013	0.0027	0.030 ± 0.014 (100) 0.014-0.055	0.031 ± 0.014 (100) 0.0080-0.051	0.034 ± 0.0054 (100) 0.028-0.041	0.020 ± 0.0068 (100) 0.0098-0.026
199	2,2',3,3',4,5,6,6'	0.0001	0.0003	0.0051 ± 0.0022 (89) 0.0022-0.0091	0.0011 ± 0.0006 (71) 0.0003-0.0019	0.0013 ± 0.0002 (100) 0.0010-0.0016	0.0008 ± 0.0002 (67) 0.0005-0.0010
201	2,2',3,3',4,5,5',6'	0.0069	0.0075	0.23 ± 0.11 (100) 0.093-0.47	0.29 ± 0.12 (100) 0.066-0.49	0.26 ± 0.026 (100) 0.21-0.29	0.16 ± 0.028 (100) 0.087-0.19
202	2,2',3,3',5,5',6,6'	0.0021	0.0024	0.095 ± 0.051 (100) 0.035-0.20	0.083 ± 0.034 (100) 0.019-0.14	0.099 ± 0.011 (100) 0.082-0.11	0.055 ± 0.011 (100) 0.029-0.072
205	2,3,3',4,4',5,5',6	0.0004	0.0005	0.0061 ± 0.0031 (89) 0.0030-0.013	0.0077 ± 0.0033 (100) 0.0018-0.013	0.0073 ± 0.0017 (100) 0.0043-0.011	0.010 ± 0.0017 (100) 0.0072-0.014
	Sum of Octa-chlorobiphenyls	0.032	0.035	0.81 ± 0.30 (100) 0.42-1.3	0.82 ± 0.36 (100) 0.19-1.5	0.81 ± 0.10 (100) 0.64-0.94	0.54 ± 0.10 (100) 0.32-0.71
206	2,2',3,3',4,4',5,5',6	0.0018	0.0013	0.020 ± 0.0077 (89) 0.010-0.033	0.043 ± 0.022 (100) 0.0085-0.090	0.036 ± 0.0070 (100) 0.024-0.048	0.026 ± 0.011 (100) 0.017-0.042
207	2,2',3,3',4,4',5,6,6'	0.0001	0.0001	0.0018 ± 0.0007 (89) 0.0012-0.0030	0.0027 ± 0.0011 (100) 0.0008-0.0041	0.0030 ± 0.0006 (100) 0.0020-0.0041	0.0026 ± 0.0008 (67) 0.0015-0.0037
	Sum of Nona-chlorobiphenyls	0.0019	0.0014	0.020 ± 0.0098 (100) 0.0022-0.036	0.046 ± 0.023 (100) 0.0093-0.093	0.039 ± 0.0075 (100) 0.026-0.052	0.028 ± 0.012 (100) 0.017-0.046
	Total PCB	0.63	0.44	16. ± 7.7 (100) 7.6 - 31.	10. ± 2.9 (100) 2.7 - 20.	11. ± 2.0 (100) 8.3 - 13.	7.6 ± 1.8 (100) 4.2 - 11.

Mean ± Standard Deviation (% occurrence)
Range

environmental levels of PCBs. However, in any study which relates exposure to effects it is relevant to know the bioaccumulated levels of specific congeners in addition to that of total PCBs. The more toxic congeners among hexa- and heptachlorobiphenyls tend to persist and become enriched in fauna (Safe *et al.* 1982, Ballschmiter *et al.* 1978), as indicated in Figure 2. At a given level of total PCBs, concentrations of the more toxic components may vary widely among different organisms.

The proportions of congeners were notably different for PCB mixtures in sediment and various fauna from Mud Island. These differences were most apparent when the congener concentrations in fauna were grouped by homolog and expressed as ratios to the corresponding values for sediment. The resulting distribution coefficients (K_d) were plotted for oligochaete/sediment, carp/-sediment, and ducks/sediment (Fig. 3). The K_d values for oligochaete/sediment range near unity, indicating that in oligochaetes there was little, if any, biomagnification of sediment PCBs as a whole. However, the plot for oligochaetes shows relatively lower concentrations of tri- through pentachlorobiphenyls and slightly higher levels of hepta- and octachlorobiphenyls than in sediment. In contrast, the carp and duck K_d plots (mean values) indicate much greater elevations of PCB levels over those in sediment. The K_d values for carp homologs ranged from 11 for trichlorobiphenyls to 47 for octachlorobiphenyls. In ducks the range was much greater, from 2.7 from dichlorobiphenyls to 43 for octachlorobiphenyls. Apparently in ducks there was more selective bioaccumulation and/or retention of the heavier, more chlorinated congeners than in carp or oligochaetes.

Although the source of PCBs in oligochaetes was clearly the Mud Island sediment they inhabited, it is less certain where carp and ducks obtained the bulk of their PCB content. Carp may experience varying exposures to PCBs through feeding within different areas of the Detroit River system. However, much greater variability of exposures is likely for ducks due to their seasonal migrations and the greater diversity of food items available to them. Further complicating the effects of varying exposure on PCB composition are the biological differences in uptake and accumulation that may occur in different species.

In order to evaluate sediment as a direct source of PCBs in fauna, we sought to identify congeners that appear to be least affected by selective accumulation processes in different organisms. We expected that the ratios of such congeners would provide a basis for comparing PCB mixtures that was independent of concentration differences. As a first step we compared the variability of all PCB ratios in Mud Island samples. Ballschmiter *et al.* (1978) used a similar approach to identify conservative ratios of "recalcitrant" congeners for purposes of estimating past loadings of PCB Aroclors 1254 and 1260 to the environment. Similarly, we found that six PCB congeners (Fig. 2), occurring in all Mud Island samples, were most often represented in the most consistent ratios, as indicated by their low root mean square error. Three of the six congeners (peak nos. 170, 180, and 183) were major constituents of the samples (Fig. 2). Among 13 ducks studied, the six congeners comprised 22.1–34.5% of the total PCB mass. Their structures are shown in Table 4. One compound, 2,2′,3,3′,4,4′5-heptachlorobiphenyl (peak no. 170), which constitutes 9.5% (mean value) of the PCB mass in 13 ducks, is known to induce hepatic microsomal monoxygenase enzymes of both the PB- and MC-type (Parkinson *et al.* 1981, Parkinson and Safe 1981). The capacity of compounds to induce the MC-type or aryl hydrocarbon hydroxylase (AHH) enzymes is thought to be highly correlated with their toxicity (Poland *et al.* 1979, Safe *et al.* 1982). Another of the six congeners, 2,2′,3,4,4′,5,5′-heptachlorobiphenyl (peak no. 180), which comprises 12.0% of the duck PCBs, is also likely to be a AHH inducer based on its structural characteristics (Safe *et al.* 1982). Two additional congeners, 2,2′,3,4,4′,5′-hexachlorobiphenyl (peak no. 138) and 2,3,3′,4,4′,5-hexachlorobiphenyl (peak no. 156), which are known to be AH inducers (Safe *et al.* 1982), also form consistent ratios with the six compounds above. The combined toxicity and persistence of these congeners increases their potential for adverse effects on ducks and other fauna that bioaccumulate them selectively. Most of the same congeners were prominent in human subjects exposed to PCBs in the Yusho incident (Bandiera *et al.* 1984).

We used the six congeners to form three nonredundant ratios identified here by their peak numbers as 180/170, 183/172, and 194/195. The magnitude and variability of the ratios in sediment, oligochaetes, carp, and ducks were compared as an indication of similarity within and between sample types. The results of a multivariate analysis of variance indicated no significant differences ($\alpha = .05$) between the three ratios in sediment, oligochaetes, and nine carp. However, carp ratios were signifi-

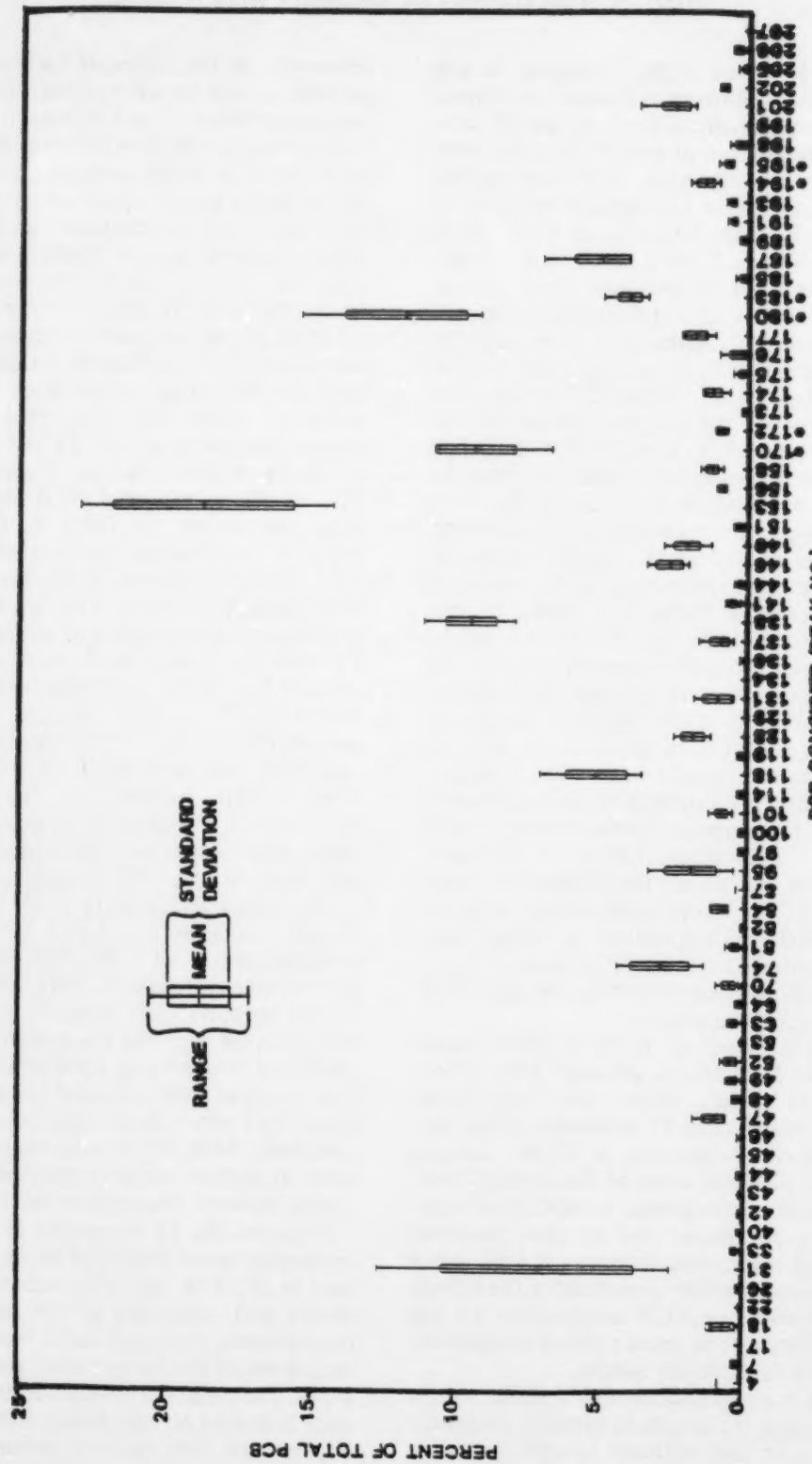

FIG. 2. Aggregate percent of PCB congeners in 13 scaup and goldeneye ducks. Asterisks indicate six congeners forming conservative ratios.

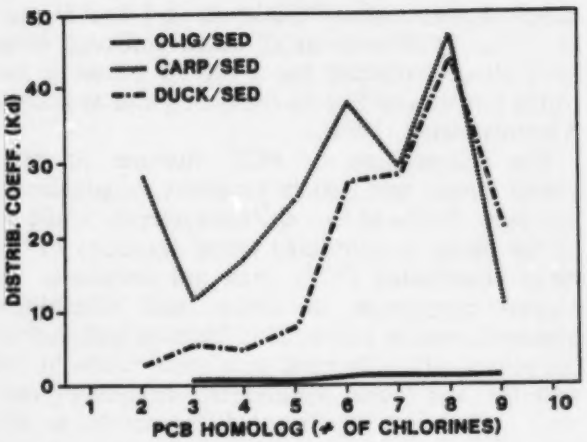

FIG. 3. Median distribution coefficients (K_d) of PCB homologs for ducks/sediment, carp/sediment, and oligochaetes/sediment.

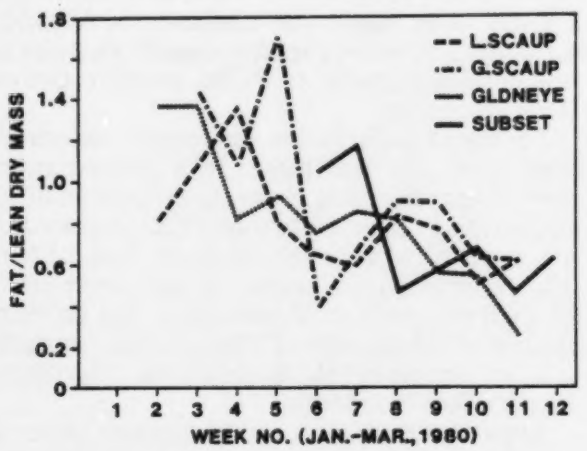

FIG. 4. Fat/lean dry mass versus week collected for 169 ducks (R. D. Drobney, 1983, personal communication, University of Maryland, Frostburg, MD) and the analyzed subset of 13.

cantly different (α = .05) from those in the 13 ducks. Within the three duck species, the ratio differences were not significant (α = .05).

While these results are very limited, they suggest the following interpretation. We infer that the PCB compositions of both oligochaetes and carp were strongly influenced by exposure to Mud Island sediment since their ratios were very similar. The different ratios which occurred in ducks suggest that their PCBs were derived from other sources as well. Also, the ducks were collected 2 years prior to the other samples. However, the striking consistency of these ratios among the three species of migratory ducks suggests a different explanation: that their PCBs were largely from a common source (possibly Mud Island sediment), but were proportioned differently as a group by more selective uptake and/or retention of congeners. Their distinctive pattern may be seen in the plots of homolog distribution coefficients described earlier (Fig. 3). The duck PCBs were consistently more enriched in hexa-, hepta-, and octachlorobiphenyls than were PCBs in other system compartments, including water and seston.

In order to investigate the possible influence of accelerated fat metabolism on the PCB content of wintering ducks, we examined the relationship between PCB concentrations in lipid and the percentage of lipid in 13 duck carcasses during the February–March period. Tissue composition data collected for all 169 Detroit River scaups and goldeneyes (R. D. Drobney 1983, personal communication, University of Maryland, Frostburg, MD) indicated that the ratio of fat/lean dry mass declined during the January–March period (Fig. 4). Most of the decline occurred in January, and reached a plateau in mid-February for the population as a whole. A smaller increase in percent fat then occurred during late February through early March. The latter trend may have represented an increase in the number of transient birds with higher fat content, or improved feeding conditions. Also, it may be explained by a relative decrease in lean dry mass, as occurs in other wintering duck species (Reinecke *et al.* 1982, Peterson and Ellarson 1978). However, the tendency toward increasing fat/lean mass was not apparent in the subset of 13 ducks that we analyzed (Fig. 4).

We used a linear regression analysis to relate the concentration of PCBs in lipid to the percentage of lipid in 13 carcasses (lipid/wet weight). This analysis was applied to both total PCB mass and the fraction of six congeners that were selected as most conservative. The results (Fig. 5) showed that concentrations of both were inversely correlated to percent lipid (r = 0.76 and 0.71, respectively). Moreover, the six-congener fraction (PCB_f) as a percentage of total PCBs (PCB_t) appeared to increase as the percent lipid declined. Based on the regression lines, PCB_f/PCB_t would be predicted to

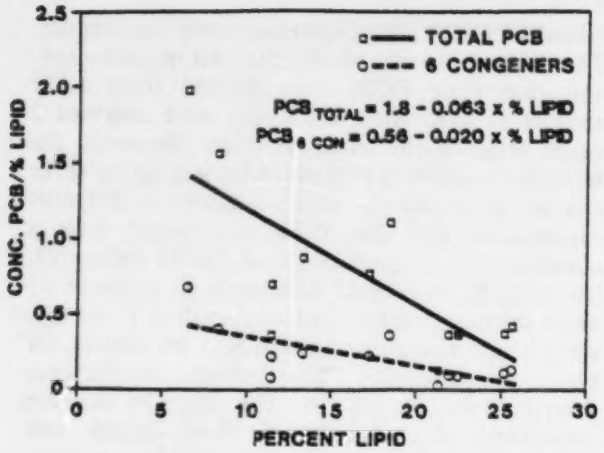

FIG. 5. Linear regression analysis of total PCBs/% lipid and six congeners/% lipid on percent lipid in 13 ducks.

increase slightly from 0.25 at 25% lipid to 0.31 at 5% lipid. In other words, PCBs as a whole behaved somewhat less conservatively than the six-congener fraction during this period.

Stickel (1973) noted that, despite cyclic increases in lipid metabolism, loss of fat-soluble contaminants in birds are usually slow. White *et al.* (1981) attempted a similar regression analysis of DDE and dieldrin with percent lipid in wintering blue-winged teal, but the results were not significant due to the low concentrations of pesticides present.

CONCLUSIONS

Wintering scaup and goldeneye ducks which foraged on contaminated sediments near Mud Island in the lower Detroit River were exposed to organochlorines, including sediment PCB concentrations on the order of 0.63 mg/kg. Similar concentrations were found in benthic oligochaetes, confirmed 2 years earlier as a major component of duck diets at this site. Body burdens of PCBs in the ducks, ranging from 2.7 to 20 mg/kg in the carcass and from 38 to 89 mg/kg in the lipid fraction, were high relative to 1979 means of < 1 mg/kg for wing pools of mallards and black ducks from the Atlantic flyway (Cain 1981). They also exceeded most 1979–1980 levels of PCB in 17 species of dabbling and diving ducks, including greater scaups and goldeneyes, from New York state (Kim *et al.* 1984). Levels in Detroit River ducks were more comparable to those in greater scaup and goldeneyes wintering on the Baltic Sea (Falandysz and Szefer 1982). Adult carp from Mud Island contained slightly higher PCB levels of 7.6 to 31 mg/kg. Total PCB levels in all ducks and carp from Mud Island exceeded the 2 mg/kg guideline for edible fish established by the U.S. Food and Drug Administration (1984).

The composition of PCB mixtures in Mud Island ducks, and that in sediment, oligochaetes, and carp, followed two distinct patterns. While all of the fauna accumulated larger fractions of the more chlorinated PCBs than did sediment, the highest proportion of hepta- and octachlorobiphenyls was in ducks. This fraction included six congeners which formed consistent ratios in the sediment and fauna. Multivariate analysis of variance indicated a significant difference ($\alpha = .05$) between three ratios formed from the six congeners in carp and in ducks. There was no significant difference among the three duck species.

The greater enrichment of heavier PCB congeners in ducks may have resulted from a more selective process of bioaccumulation and/or from dietary exposure to different PCB sources elsewhere. On the other hand, the similarity of homolog ratios in all three duck species suggests exposure to one dominant source of PCBs, possibly Detroit River sediments.

For the 13 ducks, lower fat content was correlated ($\alpha = .05$) with higher PCB concentrations over a 2-month period. Since the proportion of six conservative congeners in total PCBs increased by 6% as predicted fat levels decreased from 25% to 5%, fat mobilization seemed to have some effect on PCB composition. To the extent that differential loss of less persistent PCBs occurred during fat loss, an increase in the ratio of the six congeners to total PCBs was expected.

Some of the principal organochlorines observed in sediment, oligochaetes, carp, and ducks from Mud Island were compounds of documented toxicity. These included pesticides as well as nine PCB congeners that comprised roughly a third of the total PCB mass in ducks. Among the latter were congeners which induce aryl hydrocarbon hydroxylase (AHH) enzymes in the manner of other known toxins (Safe 1980). Any toxicity of these to scaup and goldeneye ducks remains unknown. Although we are not aware of any adverse conditions among Detroit River ducks which might be attributed to contaminant exposures, such effects would seem more likely to occur when ducks are stressed by cold weather and starvation. It is important to recognize that the contaminants reported here in ducks are likely to rep-

resent only part of their total exposure to potentially toxic substances, both organic and inorganic, which occur in Detroit River sediments. Due to biological mixing of recent sediments these substances continue to be available to bottom-feeding ducks and other fauna. As game species, scaups and goldeneyes contaminated by Detroit River sediments may also present a hazard to human populations throughout their extensive flyway.

ACKNOWELDGMENTS

We owe special thanks R. D. Drobney for use of his unpublished data in Table 2 and Figure 4 of this paper. We also thank all other contributors to this work, especially J. Rood, S. Rood, J. Rathbun, S. Mathews, and M. Kasprzyk of Cranbrook Institute of Science, D. Dolan and M. Mullin of the U.S. Environmental Protection Agency, and K. McGunagle, D. Griesmer, R. Brown, and D. Caudill of Computer Sciences Corporation. The project was supported by EPA Grant #CR810232-01 to Cranbrook Institute of Science.

REFERENCES

Ax, R. L., and Hansen, L. G. 1975. Effects of purified PCB analogs on chicken reproduction. *Poultry Sci.* 54:895–900.

Ballschmiter, K., and Zell, M. 1980. Analysis of polychlorinated biphenyls (PCBs) by glass capillary gas chromatography. Composition of technical Aroclor- and Clophen-PCB mixtures. *Fres. Z. Anal. Chem.* 302:20–31.

_____, Zell, M., and Neu, H. J. 1978. Persistence of PCBs in the ecosphere: Will some PCB-components "never" degrade? *Chemosphere* 7:173–176.

Bandiera, S., Farrell, K., Mason, G., Kelley, M., Romkes, M., Bannister, R., and Safe, S. 1984. Comparative toxicities of the polychlorinated dibenzofuran (PCDF) and biphenyl (PCB) mixtures which persist in Yusho victims. *Chemosphere* 13:507–512.

Cain, B. W. 1981. Nationwide residues of organochlorine compounds in wings of adult mallard and black ducks, 1979–1980. *Pest. Monit. J.* 15:128–134.

Choi, W. W., and Chen, K. Y. 1976. Associations of chlorinated hydrocarbons with fine particulates and humic substances in nearshore surficial sediments. *Environ. Sci. Technol.* 10:782–786.

Crump-Wiesner, H. J., Feltz, H. R., and Yates, M. L. 1973. A study of the distribution of polychlorinated biphenyls in the aquatic environment. *J. Res. U.S. Geol. Surv.* 1:603–607.

Cummins, K. W., and Wuycheck, J. C. 1971. *Caloric equivalents for investigations in ecological energetics.* Int. Assoc. Theor. Appl. Limnol., Comm. No. 18.

Custer, T. W., and Heinz, G. H. 1980. Reproductive success and nest attentiveness of mallard ducks fed Aroclor 1254. *Environ. Poll. Ser. A.* 21:313–318.

Drobney, R. D., Jones, J. J., and Noseworthy, S. M. 1982. *The effects of winter navigation on waterfowl and benthic communities.* Final Report to the U.S. Fish and Wildlife Service, Grant DOI-C-14-16-009, Patuxent Wildlife Research Center, Laurel, Maryland.

Duinker, J. C., Hillebrand, M. T. J., Palmork, K. H., and Wilhelmsen, S. 1980. An evaluation of existing methods for quantitation of polychlorinated biphenyls in environmental samples and suggestions for an improved method based on measurement of individual components. *Bull. Environ. Contam. Toxicol.* 25:956–964.

Environment Canada. 1979. *Analytical Methods Manual.* Inland Waters Directorate, Water Quality Branch, Ottawa, Canada.

Falandysz, J., and Szefer, P. 1982. Chlorinated hydrocarbons in diving ducks wintering in Gdansk Bay, Baltic Sea. *The Science of the Total Environment* 24:119–127.

Fallon, M. E., and Horvath, F. J. 1983. *A preliminary assessment of pollutants in sediment depositional areas of the Detroit River.* Report to the U.S. Environmental Protection Agency, Grant R-005666-01. Regional Office, Region V, Chicago, Illinois.

Hague, R., Schmedding, D., and Freed, V. 1974. Aqueous solubility, adsorption and vapor behavior of polychlorinated biphenyl Aroclor 1254. *Environ. Sci. Technol.* 8:139–142.

Haseltine, S. D., and Prouty, R. M. 1980. Aroclor 1242 and reproductive success of adult mallards (*Anas platyrhynchos*). *Environ. Res.* 23:29–34.

Heath, R. G., Spann, J. W., Kreitzer, J. F., and Vance, C. 1972. Effects of polychlorinated biphenyls on birds. In *Proc. 15th Int. Ornithol. Congress*, pp. 475–485.

Hutzinger, O., Safe, S., and Zitko, V. 1974. *The Chemistry of PCBs.* Cleveland, Ohio: CRC Press, Inc.

Karickhoff, S. W., and Morris, K. R. 1985. Impact of tubificid oligochaetes on pollutant transport in bottom sediments. *Environ. Sci. Technol.* 19:51–56.

Kim, K. S., Pastel, M. J., Kim, J. S., and Stone, W. B. 1984. Levels of polychlorinated biphenyls, DDE and mirex in waterfowl collected in New York state, 1979–1980. *Archiv. Environ. Contam. Toxicol.* 13:373–381.

Mullin, M. D., Pochini, C. M., Safe, S. H., and Safe, L. M. 1983. Analysis of PCBs using specific isomer high resolution capillary gas chromatography. In *PCBs: Human and Environmental Hazards*, ed. F. M. D'Itrie and M. A. Kamrin, pp. 165–176. Boston: Butterworth Publishers.

_____, Pochini, C. M., McCrindle, S., Romkes, M., Safe, S. H., and Safe, L. M. 1984. High-

resolution PCB analysis: synthesis and characterization of all 209 PCB congeners. *Environ. Sci. Technol.* 18:468–476.

Murphy, P. G. 1972. Sulfuric acid for cleanup of animal tissues for analysis of acid-stable chlorinated hydrocarbon residues. *J. Assoc. Offic. Anal. Chem.* 55:1360–1362.

Parkinson, A., and Safe, S. 1981. Aryl hydrocarbon hydroxylase induction and its relationship to the toxicity of halogenated aryl hydrocarbons. *Toxicol. Environ. Chem.* 4:1–46.

_____, Robertson, L., Safe, L., and Safe, S. 1981. Polychlorinated biphenyls as inducers of hepatic microsomal enzymes: effects of di-ortho substitution. *Chem. Biol. Interact.* 31:1–12.

Peterson, S. R., and Ellarson, R. S. 1978. p,p'-DDE, polychlorinated biphenyls and endrin in Oldsquaws in North America, 1969–73. *Pest. Monit. J.* 11:170–181.

Poland, H., Greenlee, W. F., and Kende, A. S. 1979. Studies on the mechanism of toxicity of the chlorinated dibenzo-p-dioxins and related compounds. *Ann. N.Y. Acad. Sci.* 320:214–230.

Reinecke, K. J., Stone, T. L., and Owen, R. B. 1982. Seasonal carcass composition and energy balance of female black ducks in Maine. *Condor* 84:420–426.

Robbins, J. A. 1982. Stratigraphic and dynamic effects of sediment reworking by Great Lakes zoobenthos. *Hydrobiologia* 92:611–622.

Rofritz, D. J. 1977. Oligochaeta as a winter food source for the Oldsquaw. *J. Wildl. Manage.* 41:590–591.

Safe, S. 1980. Metabolism, uptake, storage and bioaccumulation. In *Halogenated Biphenyls, Terphenyls, Naphthalenes, Dibenzodioxins and Related Products*, ed. R. Kimbrough, pp. 81–107. Amsterdam: Elsevier Publishing.

_____, Robertson, L., Sawyer, T., Bandiera, S., Safe, L., Parkinson, A., Campbell, M. A., and Mullin, M. D. 1982. PCBs: structure-activity relationships. In *Advances in Exposure, Health and Environmental Effects Studies of PCBs*, pp. 229–248. Report to the U.S.Environmental Protection Agency, Contract 69-01-6554. ICAIR Life Systems, Inc., Cleveland, Ohio.

Smith, V. E., Spurr, J. S., Rathbun, J. E., Filkins, J. C., and Rood,J. T. 1985. Organochlorine contamination of sediments and biota in the nearshore Great Lakes. U.S. Environmental Protection Agency Project Report (CR810232-01). In progress.

Stickel, L. F. 1973. Pesticide residues in birds and mammals. In *Environmental Pollution By Pesticides*, ed. C. A. Edwards, pp. 254–312. New York: Plenum Press.

Stonard, M. D., and Grieg, J. B. 1976. Different patterns of hepatic microsomal enzyme activity produced by administration of pure hexachlorobiphenyl isomers and hexachlorobenzene. *Chem.-Biol. Interact.* 15:365–379.

Thompson, J. F. 1974. *Analysis of pesticide residues in human and environmental samples.* U.S. Environmental Protection Agency, Research Triangle Park, North Carolina.

U.S. Food and Drug Administration. 1984. Polychlorinated biphenyls (PCBs) in fish and shellfish; reduction of tolerances; final decision. *Federal Register* 49(100):21514–21520.

White, D. H., King, K. A., Mitchell, C. A., and Krynitsky, A. J. 1981. Body lipids and pesticide burdens of migrant blue winged teal. *J. Field Ornithol.* 52:23–28.

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.